

Determination of Hydrogen by Slow Combustion Over Platinum in Excess Oxygen

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The accuracy and reproducibility of the determination of hydrogen by combustion with excess oxygen over a hot platinum helix (slow combustion) have been experimentally measured. The combustion of a pure hydrogen gave the observed stoichiometric relationship, $H_2 + 0.4996 O_2 \rightarrow 1.4996$ contraction. The ideal relationship, corrected for the deviations of hydrogen and oxygen, is $H_2 + 0.4994 O_2 \rightarrow 1.4994$ contraction. Uncorrected, the method gave these results: Hydrogen calculated from the contraction, 99.98 ± 0.03 percent; hydrogen from oxygen consumed, 99.91 ± 0.13 . Corrected, these results became 100.02 ± 0.03 and 100.03 ± 0.13 , respectively.

1. Introduction

This is one of a series of papers [1 to 10]² reporting experimental measurements of the accuracy and reproducibility of existing methods of gas analysis, by the analysis of gases of critically known purity or standard gas mixtures. This paper deals with the determination of hydrogen by slow combustion. In work of this kind, the greatest single burden usually is the preparation of the gas of known purity and the determination of its purity to a significance greater than the capability of the analytical method under investigation. All too often, the behavior of a method is reported in terms of the analysis of a "pure" substance or "synthetic mixture," and the results accepted as fact, even when no conclusive evidence of purity or known composition has been presented. This is unfortunate, for no more direct means exists to verify an analytical method than to make repeated analyses of a substance or substances of known composition. If the analyses can be made by many analysts using an identical procedure during a considerable time, so much the better. The accuracy and reproducibility to be expected with such a diffuse effort, which gives the picture of what generally may be expected, are never so favorable as those obtained in a single laboratory by one careful worker. The work reported here, however, is of this more restricted nature.

2. Hydrogen Used for Analysis

The hydrogen for this work was obtained from the electrolytic battery generating the hydrogen used for liquefaction at the Bureau. When this battery has been operating for some time, all air is displaced, and the only impurity occurring in the hydrogen is oxygen, which is removed by passage over hot platinum. The purity of the hydrogen was checked at the plant by a special thermal-conductivity apparatus sensitive to less than 0.01 percent oxygen. Hydrogen so prepared was passed at atmospheric pressure through a previously evacuated in-seal con-

denser equipped with a glass-wool filter and immersed in liquid hydrogen. The saturation pressure of any higher-boiling impurities is negligible at this temperature. (For oxygen it is of the order of 10^{-15} mm Hg, and the filter removes any fine crystals from the incoming stream of gas.) If helium is not an impurity, this is an effective way of preparing pure hydrogen. Hydrogen so prepared should contain less than 0.00001 percent by volume of higher-boiling impurities. Thus the total impurity of the hydrogen used in this work was several orders of magnitude less than the occasion demanded.

The oxygen used for combustion was obtained from rectification of liquid air. The inert impurity was determined as the residue after absorption in alkaline pyrogallol. The nitrogen in the buret at the beginning of each analysis was prepared initially from air by five complete passages of the gas into the pipet containing alkaline pyrogallol and thereafter by removal of oxygen from the products of combustion.

3. Analytical Procedure

The apparatus described by Shepherd [11] was used for the analysis. The procedure was as follows:

1. Nitrogen (about 60 ml) was prepared, measured, and stored in the pipet containing the solution of alkaline pyrogallol (pyro pipet).

2. Oxygen (about 60 ml) of known composition was measured and transferred to the slow-combustion pipet.

3. Hydrogen (about 60 ml) was measured and slowly (not more than 10 ml/min) passed into the combustion pipet with platinum spiral heated to a cherry-red color. Gas from the arm of the manometer connecting to the distributor was displaced to the buret and transferred to the combustion pipet. Four complete passages between the buret and combustion pipet were made.

4. The residue from the combustion was measured and the contraction computed.

5. Nitrogen from the pyrogallol pipet was transferred to the buret, and the oxygen was removed from the combined nitrogen and residue from the combustion by five complete passages into the pyro-

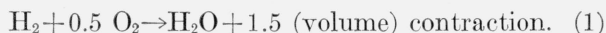
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² Figures in brackets indicate the literature references at the end of this paper.

gallol solution. The residual nitrogen was measured, and from this the excess oxygen and the oxygen consumed were computed.

4. Stoichiometry and Discussion of Errors

If the reaction involves only hydrogen and oxygen, and is complete; if the gases are all ideal gases; if there are no gains or losses through solution or otherwise except the quantitative absorption of oxygen in the pyrogallol solution, and the contraction caused by condensation of the water formed; and if there are no errors of manipulation or observation during the analysis, the observed values for the analysis would correspond to the ideal stoichiometric equation



Actually, the observed values did not correspond to this equation. Instead, the average values of 20 analyses are expressed by the volume equation



An explanation of the observed values involves the discussion of various errors. In this discussion, reference will be made to the stoichiometric data given in table 1. Columns 1 and 2 of this table give the data for observed contraction per sample and oxygen consumed per sample, from which eq (2) was derived.

TABLE 1. Observed stoichiometric ratios

Analysis No.	1 Contraction per sample	2 Oxygen consumed per sample	3 N ₂ balance	4 Corrected oxygen consumed per sample
			ml	
1.....	1.4993	0.4989	-0.02	0.4993
2.....	1.5000	.5004	+ .02	.5000
3.....	1.5000	.4990	-.06	.5000
4.....	1.4995	.4990	-.03	.4995
5.....	1.4997	.5002	+ .06	.4992
6.....	1.4990	.4987	-.02	.4990
7.....	1.5001	.4996	-.03	.5001
8.....	1.4997	.4992	-.03	.4997
9.....	1.4998	.5011	+ .08	.4998
10.....	1.4999	.4996	-.02	.4999
11.....	1.4994	.5002	+ .05	.4994
12.....	1.4993	.4995	+ .01	.4993
13.....	1.4999	.5002	+ .02	.4999
14.....	1.4986	.4982	-.02	.4986
15.....	1.4999	.4989	-.06	.4999
16.....	1.4990	.5010	+ .11	.4990
17.....	1.4997	.4994	-.02	.4997
18.....	1.5006	.5001	+ .01	.4999
19.....	1.4991	.4986	-.03	.4991
20.....	1.5003	.4993	-.06	.5003
Average.....	1.49964	0.49956	-----	0.49958
Average deviation.....	±0.00039	±0.00064	-----	±0.00034

5. Deviation of the Gases from Ideality

The usual chemical volumetric gas analysis involves the measurement of various mixtures of gases. The sample is ordinarily a mixture which is progressively simplified by the removal of one or more constituents at a time. The products of combustion are mixtures. Thus, correction for deviation from ideality is quite

difficult, for while deviations for many of the separate gases have been measured, there is no law to predict their behavior in mixtures, and the deviations significant to the analysis must be measured. The present analysis is an exception. Every gas measured throughout is an approximately pure one. Thus, the gases measured at each step of the analysis are (in order) nitrogen, oxygen, hydrogen, oxygen, and nitrogen. A stoichiometric equation accounting for the deviations from ideality at 1 atm and 25° C (for H₂, $PV/nRT=Z=1.0006$ [14]; for O₂, $Z=0.9994$ [15]) may accordingly be written: $1.0006 \text{H}_2 + 0.5 (0.9994) \text{O}_2 \rightarrow 1.5003$ contraction or,



This correction alone brings the ideal eq (1) into better agreement with eq (2), for the observed values.

6. Other Considerations

By comparison of eq (2) and (3) it becomes evident that eq (2) would have been identical with eq (3) if the 0.0002 volume less oxygen had been consumed; for then the contraction would also have been 0.0002 volume less. If this correlation is significant, it indicates that the only appreciable error sustained in the combustion was the reduction of slightly more oxygen than commensurate with the amount of hydrogen burned. Several possible fates of this oxygen deserve consideration.

The oxidation of nitrogen is hardly possible in this analysis. Even when air (with high partial pressure of nitrogen) was burned with hydrogen, NO₂ was not found to have been formed during the procedure used for combustion. The only nitrogen present during this combustion was at very low partial pressure, occurring to the extent of 0.09 percent in the oxygen used (in actuality, most of this "nitrogen" was probably argon). Nitrogen dioxide when formed reacts almost completely with the wet mercury and is accordingly observed as part of the contraction. Such an error seems not to have occurred in this instance.

The formation of a small amount of mercuric oxide might have accounted for the slightly high oxygen consumption and an equal increase in contraction. Perhaps a small amount of hydrogen peroxide may have been formed at the hot platinum spiral, then removed from the gas phase by reduction with lubricant in the stopcocks between the combustion pipet and the buret; or a small amount of ozone may have formed at the hot wire, then formed addition products with stopcock lubricant. Loss of oxygen by solution in water formed during combustion was calculated to be insignificant.

Under the conditions of the analysis, an average of less than 0.01 ml of carbon monoxide may have been generated during the absorption of excess oxygen, [12]. This carbon monoxide would not have entered into the next combustion with reuse of the residual nitrogen; but if it occurred, it would have appeared as nitrogen at the last step in the procedure.

This would have made the excess oxygen appear too small and the oxygen consumed correspondingly too large. Indeed, a comparison of eq (2) with eq (3) does show observed oxygen consumed to be high; but this explanation does not fit the case because when oxygen consumed is corrected for nitrogen off-balance the value is insignificantly changed, in the wrong direction. This correction eliminates the error in oxygen consumed caused by the generation of carbon monoxide.

The nitrogen balance, or total loss or gain of gas during each complete analysis, is determined by comparing the nitrogen originally measured with the residual nitrogen. These data are given in column 3 of table 1. While the sum of the gains and losses is algebraically almost zero for the series of analyses (the observed cumulative loss was 0.04 ml, or an average of 0.0002 ml per analysis), and while many of them are near the expected error of volume measurement (± 0.02 ml), nevertheless, there are more losses than gains, and the losses are somewhat more systematic. Every time a loss of nitrogen occurred, the oxygen consumed was found to be low; whereas with every gain of nitrogen the consumed oxygen was high (with a single exception, analysis 12). If the analyses are corrected individually for this off-balance of nitrogen to adjust the oxygen consumed, 15 of the 20 show improved values for oxygen consumed (column 4, table 1). Of these, 15, 12 occur when the nitrogen balance shows a loss. This seems significant, and indicates complete absorption of excess oxygen, complete combustion of the sample, and no significant production of carbon monoxide. Since the solution of alkaline pyrogallol was in equilibrium with nitrogen before and after each absorption, and is one of the best reagents with respect to exchange of inerts by sorption and desorption [13], what seems to be a slight apparent loss of nitrogen could hardly have been caused by physical solution of nitrogen.

When the oxygen consumed is corrected for nitrogen balance on the assumption that the latter was a measure of the error made in the measurement of excess oxygen, the observed stoichiometric eq (2) is not changed significantly, but the reproducibility of the oxygen value is considerably improved. The previous discussion may therefore seem partly gratuitous; but the errors considered may affect individual analyses rather than the average of a large group—and usually only a few analyses of a single sample are made, so that the possibility of such errors should always be kept in mind.

The application of this correction renders the value for oxygen consumed independent of the inert content of the oxygen. Since it does not appreciably change the average oxygen value, assurance is afforded that the analysis of the oxygen was accurate; or that generation of carbon monoxide by pyrogallol, if it occurred, compensated for the error in the analysis of the oxygen.

7. Analytical Data

The results of computing the analyses from the observed and corrected stoichiometric relations just discussed are given in table 2. The percentages of hydrogen calculated from the observed contraction and oxygen consumed (columns 1 and 2) average 99.975 ± 0.027 and 99.912 ± 0.126 , respectively. The observed contraction yielded more satisfactory results with respect to both accuracy and reproducibility than oxygen consumed; but this is to be expected, since there are more chances for errors in this measurement, and the arithmetic involved penalizes this measurement while favoring the measurement by contraction. The net error in oxygen consumed is multiplied by 2 in calculating hydrogen, but divided by 1.5 in calculating hydrogen from the contraction. The measurement of contraction involves the measurement of 3 gas volumes (oxygen, hydrogen, and residual oxygen) and a simple catalytic combustion in which the possibilities of side reactions and errors of sorptions are probably limited to those discussed under "other considerations." The measurement of oxygen consumed involves the measurement of 4 gas volumes (oxygen, residual oxygen, original nitrogen, and residual nitrogen), and an absorption which might include a side reaction and errors of solubility. In addition, another analysis—that made to determine the purity of the oxygen used—is also involved. Altogether, the measurement of oxygen consumed is relatively handicapped, and its analytical use as a check on the contraction is of doubtful value. If the measurement is made, it is probably advisable to correct it for nitrogen off-balance; for while this correction does not

TABLE 2. Apparent percentages of hydrogen

Analysis No.	1 Contraction per 1.5 sample	2 2 O ₂ per sample	3 2 O ₂ per sample	4 Contraction per 1.4994 sample	5 2.0024 O ₂ per sample	6 2.0024 O ₂ per sample
1.....	99.95	99.79	99.86	99.99	99.90	99.96
2.....	100.00	100.07	100.00	100.04	100.20	100.12
3.....	100.00	99.77	100.00	100.04	99.92	100.12
4.....	99.97	99.80	99.90	100.01	99.92	100.04
5.....	99.98	100.03	99.84	100.02	100.16	100.04
6.....	99.93	99.73	99.80	99.97	99.86	99.92
7.....	100.00	99.92	100.02	100.04	100.04	100.12
8.....	99.98	99.83	99.94	100.02	99.96	100.04
9.....	99.98	100.21	99.96	100.02	100.34	100.04
10.....	100.00	99.91	99.98	100.04	100.04	100.10
11.....	99.97	100.05	99.88	100.01	100.16	100.00
12.....	99.95	99.90	99.86	99.99	100.02	100.00
13.....	100.00	100.05	99.98	100.04	100.16	100.10
14.....	99.90	99.65	99.72	99.94	99.76	99.84
15.....	100.00	99.78	99.98	100.04	99.90	100.10
16.....	99.93	100.19	99.80	99.97	100.32	99.92
17.....	99.98	99.88	99.94	100.02	100.00	100.04
18.....	100.03	100.02	99.98	100.07	100.14	100.10
19.....	99.93	99.72	99.82	99.97	99.84	99.94
20.....	100.02	99.87	100.06	100.06	99.98	100.18
Average..	99.975	99.912	99.916	100.016	100.032	100.036
Avg. deviation.	± 0.027	± 0.126	± 0.092	± 0.027	± 0.128	± 0.068

greatly change the average value (compare the 99.916 average of column 3 with 99.912 of column 2), the reproducibility is improved (± 0.092 compared with ± 0.126), and the chance for a good individual analysis is better. Correction for nitrogen off-balance really amounts to eliminating 2 of the 4 measurements involved in determining oxygen consumed; and these 2 are more subject to error than the 2 actually used, i. e., the original measurement of oxygen taken for the combustion, and the measurement of the residual oxygen. The average deviations shown in table 1 are in order of increasing deviation: 0.00034 for corrected oxygen consumed per sample, 0.00039 for contraction per sample, and 0.00064 for oxygen consumed per sample. Correspondingly, corrected oxygen consumed per sample, contraction per sample, and oxygen consumed per sample, were obtained by the combination of 2, 3, and 4 independent gas-volume measurements, respectively.

If the percentages of hydrogen are corrected for deviations from ideality, the values given in columns 4, 5, and 6 are obtained. Hydrogen from corrected contraction gives the average 100.016 ± 0.027 percent; from corrected oxygen consumed, 100.032 ± 0.128 ; and from corrected oxygen consumed adjusted for nitrogen off-balance, 100.036 ± 0.068 percent. Although adjustment for nitrogen unbalance throws the average corrected value from oxygen consumed still further above the theoretically correct result, it may be desirable because of the improved reproducibility it affords. Thus, when only one or two analyses are available, such correction may yield the more accurate result. The fact that making this adjustment changed so little the average apparent hydrogen content is evidence that a substantial portion of the observed unbalance was not from a systematic effect but represented instead nearly random distribution of the errors in the measurement of the two additional gas volumes involved when the adjustment was not made.

In attempting to decide whether or not to correct the contraction, one is tempted by the relative amounts of the differences from the known purity, disregarding sign, to make the corrections. From a practical point of view, uncorrected contraction is probably the better choice, because a reported purity of less than 100 percent is infinitely more believable than a value greater than 100. This consideration applies equally to values from uncorrected oxygen consumed. Adjustment for nitrogen off-balance is applicable and results not only in improved reproducibility but also in a nearer approach of the computed value to the known.

The application of the ideality corrections was helpful in unmasking a slightly excessive consumption of oxygen as probably the effect that compensated the observed results for the deviations from ideality. The verification of this is a subject for future study.

8. References

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